



Highly Conducting Single-Molecule Magnets with d- Interactions

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論文内容要旨

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This work mainly focused on the experimental and theoretical characterization of conducting single-molecule magnets materials. By application of the different electronic features of organic conductors and Co-based metal complex as single-molecule magnet, several new conducting single-molecule magnets materials were synthesized. The first three-dimensional conducting single-molecule magnet with unique mixed stacking structure, $(\text{TTF})_2[\text{Co}(\text{pdms})_2]$, two-dimensional metallic state single-molecule magnet of $(\text{BEDO-TTF})_3[\text{Co}(\text{pdms})_2](\text{MeCN})(\text{H}_2\text{O})$ and one-dimensional metallic state single-molecule magnet $(\text{BEDO-TTF})_4[\text{Co}(\text{pdms})_2](3\text{H}_2\text{O})$ were synthesized and studied. From one-dimensional to three-dimensional structures, we found that by increasing the dimensionality, the electronically coupling will significantly enhanced.

Chapter 1 describes the general introduction of organic conductors and their electrical conductivity in their radical forms. The single-molecule magnet was introduced by some examples. The introduction of conducting single-molecule magnets were mainly presented here and what is the current situation. Finally, introduction on the research objective.

Chapter 2 mainly focus on the three-dimensional conducting single-molecule magnet, $(\text{TTF})_2[\text{Co}(\text{pdms})_2]$. By using the quite close redox potential of TTF and single-ion magnet, $[\text{Co}(\text{pdms})_2]$, the multiple charge transfer process was observed, which cause high electrical conductivity to the very low temperature. At the same time, single-molecule magnetism behavior was observed. This is the first example with mixed stacking structure combined with multiple charge transfer and significantly single-molecule magnet.

Chapter 3 mainly focus on the newly one-dimensional metallic conducting single-molecule magnet, $(\text{BEDO-TTF})_4[\text{Co}(\text{pdms})_2](3\text{H}_2\text{O})$. This compound showed layered feature structure in two-dimensionality. The magnetic layer exhibited strong ferromagnetism above 6.5 K, below 6.5 K, the antiferromagnetism was observed. More interesting thing is that the slow magnetic relaxation below 6.5 K was observed, which means that this compound is a single-molecule magnet at antiferromagnetically state. The insulating state below 6.5 K is due to the d-pi interaction between magnetic and the conducting layer. There are few examples exhibiting antiferromagnetically single-molecule magnet due to the strong magnetic anisotropy and weak intermolecular interaction. Calculation results showed this compound showed metallic state in one direction in Fermi surface. The band energy dispersion calculation shows that Dirac cone-like electrons in this compound.

Chapter 4 mainly focus on the newly two-dimensional metallic conducting single-molecule magnet, $(\text{BEDO-TTF})_3[\text{Co}(\text{pdms})_2](\text{MeCN})(\text{H}_2\text{O})$. This compound showed layered feature structure in two-dimensionality. The magnetic layer exhibits the paramagnetic single-molecule magnet. In contrary to the $(\text{BEDO-TTF})_4[\text{Co}(\text{pdms})_2](3\text{H}_2\text{O})$, the conducting layer show two-dimensional conducting pathway. The low temperature insulating state due to the weak localization.

Chapter 5 mainly focus on the conducting single-molecule magnet, $[\beta\text{-(BEDT-TTF)}_2\text{Dy}(\text{CF}_3\text{COO})_4\text{MeCN}]_n$, the lanthanide metal ion was used for the single-molecule magnet due to high ground state spins and strong magnetic anisotropy. The semiconducting behavior was observed in conducting layer and slow magnetic

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relaxation was observed in magnetic layer. There is no significantly interaction between magnetic layer and conducting layer due to unfavorable structure packing.

Chapter 6 concluded this work.

論文審査の結果の要旨

「ムーアの法則」によれば記録容量は 1.5 年ごとに 2 倍に増加しており、さらに容量を増加させるためには古典磁石をナノサイズまで小さくする必要がある。しかしながら、古典磁石はナノサイズでは量子揺らぎのために強磁性ではなく常磁性となるために、使えなくなる。これは「ムーアの限界」と呼ばれている。このムーアの限界を超越するために、ナノサイズの分子磁石である「単分子磁石」を用いて、伝導性の分子と単分子磁石の相互作用により巨大磁気抵抗効果 (GMR) などを観測することにより、ムーアの限界を超越することが研究目的である。

古典磁石はスピンの強磁性的に 3 次元的に並ぶことから生じているが (3D 磁石)、単分子磁石は $U=|D|S^2$ (D =一軸異方性、 S =スピン量子数) の 2 極所ポテンシャルをもっていて、ブロッキング温度以下ではスピンの上向きか下向きに凍結され、磁化をかけることにより磁気ヒステリシスを示すことから、古典磁石と全く異なる機構で生じるために (0D 磁石)、21 世紀のナノ分子磁石と呼ばれている。すなわち、1 個の単分子磁石が 1 個の磁石として働くために、1 個の磁気記録素子となる。これを用いれば「ムーアの限界」を超越することが出来る。Yongbing Shen は伝導性のドナー分子である BEDO-TTF とアクセプター性の $[\text{Co}(\text{pdms})_2]$ 単分子磁石を電解酸化法により、B03 と B04 の 2 種類の電荷移動型錯体の合成に成功し、伝導電子と単分子磁石との相互作用により負の磁気抵抗効果の観測を目指した。

B03 は室温から 12.5K まで金属的な挙動を示し、それ以下では半導体転移を起こした。交流磁化率の周波数依存性を示し、5K 以下でヒステリシスを示す単分子磁石でもあった。これは世界で初めての金属的単分子磁石である。また、40K 以下では負の磁気抵抗効果を示した。これは伝導電子と単分子磁石との相互作用によるものであることを明らかにした。

B04 は 60K と 6.5K 付近の 2 箇所金属-半導体転移を示した。バンド計算の結果、60K 付近の金属-半導体転移は Dirac Cone Structure によるものであることがわかった。一方、6.5K 付近の金属-半導体的挙動は BEDO-TTF と $[\text{Co}(\text{pdms})_2]$ 間の反強磁性的相互作用であることがわかった。興味深いことに 5K 以下でヒステリシスが観測され、交流磁化率に周波数依存性が観測されることから、反強磁性的挙動よりも低い温度領域で、単分子磁石が生き延びていることがわかった。

上記の研究成果は、博士論文としてふさわしい新規性を有しており、自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって Yongbing Shen 提出の博士論文は、博士 (理学) の学位論文として合格と認める。